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(71) Applicant
Murata Manufacturing Co Ltd

(Incorporated in Japan)

26-10 Tenjin 2-chome, Nagaokakyo-shi, Kyoto-fu,
Japan

(72) Inventors

Tetsuya Dol
Takuya Miyagawa
Yasuyuki Naito
Tadashi Morimoto

(74) Agent and/or Address for Service

R G C Jenkins & Co
26 Caxton Street, London, SW1H 0RJ, United Kingdom

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(56) Documents cited
EP 0431533 A2 EP 0385365 A2 EP 0385364 A2
EP 0187960 A2 JP 620157603 A

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(54) Dielectric ceramics

(57) A dielectric ceramic composition contains 0.3 to 5.0 parts by weight of an additive composed of at least one of SiO₂, Li₂O and B₂O₃ per 100 parts by weight of a main component expressed by the following composition formula:

(1 - x - y - z - t) BaTiO₃ + xCaZrO₃ + yMgO + zMnO + tRe₂O₃, where

$$x \leq 0.06$$

$$0.005 \leq y \leq 0.08$$

$$0.005 \leq z \leq 0.02$$

$$0.005 \leq t \leq 0.02$$

(in the composition formula, Re indicates at least one of Y, Gd, Dy, Ho, Er and Yb).

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TITLE OF THE INVENTION

Dielectric Ceramic Composition

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to a dielectric ceramic composition used to obtain a monolithic type electronic component constructed by cofiring inner electrodes and ceramics, for example, a ceramic capacitor.

Description of the Prior Art

In a monolithic type electronic component such as a multilayer capacitor, a sintered body obtained by cofiring an electrode material constituting inner electrodes and dielectric ceramics is used. Meanwhile, when the multilayer capacitor is fabricated, a conventional dielectric material mainly composed of BaTiO_3 is sintered at temperatures from 1300 to 1500°C. Accordingly, a noble metal such as Pd which is not melted at such sintering temperatures has been used as an electrode material constituting inner electrodes. However, the noble metal such as Pd is very high in cost. Consequently, when the number of inner electrodes is increased so as to achieve large capacity, the cost significantly rises. This in turn has led to cost reduction being demanded.

Therefore, an attempt to use a low-cost base metal such as nickel as the electrode material constituting inner

electrodes has been made. When inner electrodes constituted by the base metal such as nickel are used, however, the electrode material constituting the inner electrodes is liable to be oxidized. Accordingly, the dielectric material must be sintered in an atmosphere of reduction. Consequently, if the dielectric material is sintered in such an atmosphere, oxygen deficiency occurs, resulting in decreased insulation resistance.

In order to solve such a problem, a non-reduction type dielectric ceramic composition in which oxygen deficiency does not easily occur even if it is sintered in an atmosphere of reduction by adding MgO and a rare earth oxide to BaTiO₃ - CaZrO₃ is proposed (Japanese Patent Laid-Open Gazette No. 157603/1987).

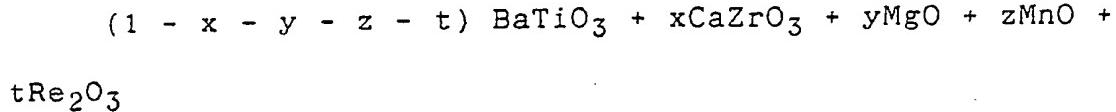
However, the dielectric ceramic composition disclosed in Japanese Patent Laid-Open Gazette No. 157603/1987 has a disadvantage in terms of its sintering properties. More specifically, it is difficult to sinter the dielectric ceramic composition unless it is sintered at temperatures of not less than 1300° C.

SUMMARY OF THE INVENTION

An object of the present invention is to provide a non-reduction type dielectric ceramic composition capable of obtaining a dielectric ceramic composition which can be sintered at relatively low temperatures and has sufficient

resistance to humidity.

The dielectric ceramic composition according to the present invention contains as a main component a component expressed by the following composition formula:



$$x \leq 0.06$$

$$0.005 \leq y \leq 0.08$$

$$0.005 \leq z \leq 0.02$$

$$0.005 \leq t \leq 0.02$$

In the composition formula, Re indicates at least one of Y, Gd, Dy, Ho, Er and Yb.

Furthermore, the non-reduction type dielectric ceramic composition according to the present invention contains 0.3 to 5.0 parts by weight of an additive composed of at least one of SiO_2 , Li_2O and B_2O_3 per 100 parts by weight of the above described main component.

The reason why x is not more than 0.06 in the above described composition formula is that the rate of variation with temperature of dielectric constant in the temperature range of - 55°C to + 125°C exceeds $\pm 15\%$ if the mixture ratio of CaZrO_3 is more than 6 mole %.

x is preferably set to not less than 0.01 nor more than 0.04. The reason for this is that the CR product is lowered, i.e., not more than 2000 when x is less than 0.01

and the change in capacitance at a high temperature (at 85° C) becomes large when x exceeds 0.04.

Furthermore, the reason why y is not less than 0.005 nor more than 0.08 is that the CR product is lowered to not more than 1000 $\Omega \cdot F$, resulting in insufficient insulation resistance, thereby to make it impossible to use the dielectric ceramic composition as a multilayer capacitor if the mixture ratio of MgO is outside of this range.

y is preferably set to not less than 0.02. The reason for this is that the CR product is lowered, i.e., not more than 2000 when y is less than 0.02.

Additionally, the reason why z is not less than 0.005 nor more than 0.02 is that the rate of variation with temperature of dielectric constant in the temperature range of - 55° C to + 125° C exceeds $\pm 15\%$ if the mixture ratio of MnO is less than 0.5 mole %, while the CR product is lowered if it exceeds 2.0 mole %. y is preferably set to not more than 0.015. The reason for this is that the CR product is lowered, i.e., not more than 2000 when y exceeds 0.015.

Moreover, the reason why t is not less than 0.005 nor more than 0.02 is that the rate of variation with temperature of dielectric constant in the temperature range of - 55° C to + 125° C exceeds $\pm 15\%$ if the mixture ratio of Re_2O_3 is less than 0.5 mole %, while the sintering properties are degraded, thereby to make it difficult to

sinter the dielectric ceramic composition at temperatures of not more than 1250°C if it exceeds 2.0 mole %.

In the present invention, the dielectric ceramic composition contains an additive composed of at least one of SiO_2 , LiO_2 and B_2O_3 to enhance the sintering properties. However, if the content of the additive per 100 parts by weight of the main component is less than 0.3 parts by weight, the dielectric ceramic composition is not sintered at a temperature of 1250°C. Consequently, not less than 0.3 parts by weight of the additive must be mixed with 100 parts by weight of the main component.

On the other hand, when the content of the additive per 100 parts by weight of the main component is more than 5.0 parts by weight, the dielectric constant ϵ is significantly lowered. Consequently, the upper limit of the content of the additive per 100 parts by weight of the main component is 5.0 parts by weight. Further, the content of the additive is preferably not more than 2.0 parts by weight per 100 parts by weight of the main component. The reason for this is that the CR product is lowered, i.e., not more than 2000 when the content of the additive exceeds 2.0 parts by weight.

In the present invention, 0.3 to 5.0 parts by weight of the above described particular additive is mixed with 100 parts by weight of the above described particular main

component, thereby to obtain a dielectric ceramic which can be sintered at temperatures of not more than 1250° C, and shows a decreased rate of variation with temperature of dielectric constant and a sufficiently large CR product as obvious from the embodiment as described later.

The above and further features of the invention are set forth with particularity in the appended claims and should become clearer from consideration of the following detailed description.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Description is now made of a non-restrictive embodiment of the present invention.

First, BaTiO₃, CaZrO₃, MgO and MnO and a rare earth oxide are weighed on the basis of respective compositions shown in Table 1 and Table 2, and an additive shown in Table 3 and Table 4 is weighed at ratios shown in the tables 3 and 4, to obtain starting materials for samples Nos. 1 to 39.

5 % by weight of a water-soluble vinyl acetate binder is added to each of the starting materials for the samples Nos. 1 to 39 prepared in the above described manner, followed by wet blending for 16 hours.

A ceramic slurry obtained by the above described blending is dried at a temperature of 150° C and then, is classified using a 60-mesh screen. Ceramic particles

obtained by the classification are formed by applying a pressure of 2 t/cm², to fabricate a disc having a diameter of 10 mm.

The disc obtained is calcined at a temperature of 300° C and in an atmosphere of air for two hours to remove the binder and then, is sintered in an atmosphere of N₂/H₂/H₂O at each of the sintering temperatures shown in the tables 3 and 4 for two hours.

An In-Ga alloy is applied to both major surfaces of each of the obtained sintered bodies of the samples and is dried, to form electrodes for measurement.

Measurements are made of the dielectric constant ϵ , tan δ , the rate of variation with temperature of dielectric constant Tc, and the insulation resistance IR of the ceramic sintered body having the above described electrodes for measurement formed therein. The conditions for the measurements are as follows:

The measurement of the dielectric constant ϵ is made by causing an AC current of 1.0 Vrms and 1.0 KHz to flow.

The measurement of tan δ is made by causing an AC current of 1.0 Vrms and 1.0 KHz to flow.

The measurement of the rate of variation with temperature of dielectric constant Tc is made in the temperature range of -55° C to +125° C and by causing an AC

current of 1.0 Vrms and 1.0 KHz to flow.

The measurement of the insulation resistance IR is made after an elapse of two minutes after a voltage of 50V was applied.

The results of the measurements are shown in Table 5 and Table 6 as described later. In addition, the CR product is also shown in the tables 5 and 6.

Compositions A to C of the additive shown in the tables 3 and 4 are as follows:

Composition A; 100 parts by weight of SiO₂

Composition B; 20 parts by weight of Ba₂O₃, 40 parts by weight of BaO, 30 parts by weight of SiO₂, and 10 parts by weight of Li₂O

Composition C; 50 parts by weight of SiO₂, 20 parts by weight of Li₂O, 10 parts by weight of BaO, 10 parts by weight of CaO, and 10 parts by weight of SrO

As can be seen from the tables 5 and 6, in the sintered body of the sample No 37, the mixture ratio of CaZrO₃ in the main component is beyond the scope of the present invention, so that the rate of variation with temperature of dielectric constant Tc is very large.

Furthermore, in the sintered body of the sample No. 6, no additive is added, so that the dielectric ceramic composition of the sample is not sufficiently sintered even at a temperature of 1300°C, thereby to make it impossible to

make the above described respective measurements.

It is found that in the sintered body of the sample No. 9, the content of the additive is high, i.e., 6.0 % by weight, so that the dielectric constant ϵ is low, i.e., 2100 and the CR product is also low.

It is found that in the sintered body of the sample No. 15, the mixture ratio of MgO in the main component is high, i.e., 9.0 mole %, so that the CR product is low, i.e., 800 ΩF . In addition, it is found that in the sintered body of the sample No. 16, MgO is not contained in the main component, so that the CR product is further lowered, i.e., 500 ΩF .

In the sintered body of the sample No. 18, the mixture ratio of the rare earth oxide in the main component is high, i.e., 2.5 mole %, so that the dielectric ceramic composition of the sample is not sufficiently sintered even at a temperature of 1300° C.

In the sintered body of the sample No. 20, no rare earth oxide is contained, so that the rate of variation with temperature of dielectric constant T_c is significantly large, i.e., -15.5 % ΔC at a temperature of 125° C. In addition, it is found that in the sintered body of the sample No. 23, the mixture ratio of MnO in the main component is high, i.e., 2.5 mole %, so that the CR product is also lowered, i.e., 800 ΩF . It is found that in the

sintered body of the sample No. 25, MnO is not contained, so that the rate of variation with temperature of dielectric constant at a temperature of -55°C is large, i.e., -16.2 %ΔC.

Additionally, it is found that in the sintered bodies of the samples Nos. 26 and 27, the rare earth oxides are respectively Ce₂O₃ and Sm₂O₃, so that the rates of variation with temperature of dielectric constant are both very large. In addition, in the sintered body of the sample No. 27, the CR product is also significantly lowered, i.e., 700 ΩF.

On the other hand, it is found that with respect to any one of the sintered bodies of the remaining samples within the scope of the present invention, the dielectric constant ϵ is relatively high, tan δ is low, i.e., not more than 0.9, the CR product representing the insulation resistance is high, i.e., not less than 1100, and the rate of variation with temperature of dielectric constant is less than ± 15 %. More specifically, any one of the sintered bodies of the samples within the scope of the present invention has superior dielectric properties.

Table 1

SAMPLE NUMBER	MAIN COMPONENT (MOLE %)					Re_2O_3	
	BaTiO_3	CaZrO_3	MgO	MnO	Re_2O_3		
					TYPE	MOLE %	
1	94	1.0	3.0	0.5	Y_2O_3	1.0	
2	93	2.0	3.0	1.0	Y_2O_3	1.0	
3	91	4.0	3.0	1.0	Y_2O_3	1.0	
4	90	5.0	3.0	1.0	Y_2O_3	1.0	
5	93	2.0	3.0	1.0	Y_2O_3	1.0	
6	93	2.0	3.0	1.0	Y_2O_3	1.0	
7	93	2.0	3.0	1.0	Y_2O_3	1.0	
8	93	2.0	3.0	1.5	Y_2O_3	1.0	
9	93	2.0	3.0	1.0	Y_2O_3	1.0	
10	89.5	2.0	6.0	0.5	Y_2O_3	1.5	
11	90	2.0	6.0	0.5	Y_2O_3	1.5	
12	87.5	2.0	8.0	1.0	Y_2O_3	1.5	
13	95.5	2.0	0.5	1.0	Y_2O_3	1.0	
14	95	2.0	1.0	1.0	Y_2O_3	1.0	
15	86.5	2.0	9.0	1.0	Y_2O_3	1.5	
16	96	2.0	---	1.0	Y_2O_3	1.0	
17	92	2.0	3.0	1.0	Y_2O_3	2.0	
18	91.5	2.0	3.0	1.0	Y_2O_3	2.5	
19	93.5	2.0	3.0	1.0	Y_2O_3	0.5	

Table 2

SAMPLE NUMBER	MAIN COMPONENT (MOLE %)					
	BaTiO_3	CaZrO_3	MgO	MnO	Re_2O_3	
					TYPE	MOLE %
20	96	0	3.0	1.0	Y_2O_3	---
21	92.5	2.0	3.0	1.5	Y_2O_3	1.0
22	92	2.0	3.0	2.0	Y_2O_3	1.0
23	91.5	2.0	3.0	2.5	Y_2O_3	1.0
24	90	2.0	6.0	0.5	Y_2O_3	1.5
25	90.5	2.0	6.0	---	Y_2O_3	1.5
26	93	2.0	3.0	1.0	Ce_2O_3	1.0
27	93	2.0	3.0	1.0	Sm_2O_3	1.0
28	93	2.0	2.0	0.5	Er_2O_3	1.0
29	91	4.0	3.0	1.0	Er_2O_3	1.0
30	89.5	2.0	6.0	1.0	Er_2O_3	1.5
31	93	2.0	3.0	1.0	Gd_2O_3	1.0
32	91	4.0	3.0	1.0	Gd_2O_3	1.0
33	93	2.0	3.0	1.0	Dy_2O_3	1.0
34	92	2.0	3.0	1.0	Ho_2O_3	1.0
35	93	2.0	3.0	1.0	Yb_2O_3	1.0
36	89	6.0	3.0	1.0	Y_2O_3	1.0
37	88.5	6.5	3.0	1.0	Y_2O_3	1.0
38	89	6.0	3.0	1.0	Er_2O_3	1.0
39	95	0	3.0	1.0	Er_2O_3	1.0

Table 3

SAMPLE NUMBER	ADDITIVE		SINTERING TEMPERATURE (°C)
	COMPOSITION	% BY WEIGHT	
1	C	0.5	1250
2	C	0.5	1250
3	C	0.5	1250
4	C	0.5	1250
5	A	0.3	1250
6	---	---	1300
7	C	1.0	1250
8	C	5.0	1250
9	C	6.0	1250
10	C	2.0	1250
11	C	1.0	1250
12	C	3.0	1250
13	B	0.5	1250
14	B	0.5	1250
15	C	2.0	1250
16	C	0.5	1250
17	B	0.5	1250
18	B	2.0	1300
19	B	0.5	1250

Table 4

SAMPLE NUMBER	ADDITIVE		SINTERING TEMPERATURE (°C)
	COMPOSITION	% BY WEIGHT	
20	A	0.5	1250
21	A	0.5	1250
22	A	0.5	1250
23	A	0.5	1250
24	B	1.0	1250
25	C	1.0	1250
26	C	1.0	1250
27	C	0.5	1250
28	C	0.5	1250
29	C	0.3	1250
30	C	0.5	1250
31	A	0.5	1250
32	A	0.5	1250
33	B	0.5	1250
34	C	0.5	1250
35	C	0.5	1250
36	B	0.5	1250
37	B	0.5	1250
38	B	0.5	1250
39	B	0.5	1250

Table 5

SAMPLE NUMBER	ϵ	tan δ (%)	CR PRODUCT (ΩF)	T C (% ΔC)			
				-55 °C	-25 °C	+85 °C	+125°C
1	3000	0.9	2100	- 9.7	- 8.0	- 8.8	- 7.2
2	2700	0.8	2300	- 5.6	- 4.7	- 6.1	- 5.4
3	3000	0.8	2000	- 3.7	- 2.0	- 9.1	- 8.0
4	3100	0.9	2000	- 4.9	- 0.8	-11.2	-10.6
5	3100	0.9	2400	- 5.6	- 4.6	- 8.7	- 7.2
6	INSUFFICIENTLY SINTERED						
7	2800	0.8	2200	- 7.1	- 5.8	- 6.9	- 5.4
8	2600	0.8	1400	- 7.0	- 4.8	- 5.0	- 4.3
9	2100	0.6	1000	- 6.6	- 4.5	- 4.2	- 3.8
10	2700	0.8	2000	- 7.2	- 5.1	- 6.4	- 6.1
11	2800	0.7	2300	- 8.8	- 6.2	- 5.6	- 4.8
12	2700	0.7	1100	- 7.9	- 5.5	- 6.4	- 5.0
13	2700	0.8	1500	- 9.6	- 7.5	- 8.6	- 7.2
14	2800	0.7	1800	- 8.2	- 6.3	- 6.8	- 5.2
15	2200	0.6	800	- 7.3	- 5.2	- 6.8	- 4.9
16	2500	0.6	500	- 5.8	- 4.8	- 5.2	- 4.0
17	2600	0.6	1200	- 5.2	- 3.8	- 6.2	- 5.1
18	INSUFFICIENTLY SINTERED						
19	3000	0.8	2000	- 5.8	- 4.9	- 8.8	- 7.6

Table 6

SAMPLE NUMBER	ϵ	tan δ (%)	CR PRODUCT (ΩF)	T C (% ΔC)			
				-55 °C	-25 °C	+85 °C	+125 °C
20	2900	0.7	2600	- 4.2	- 3.0	-12.5	-15.5
21	2800	0.6	2100	- 5.6	- 4.8	- 6.9	- 5.3
22	2500	0.5	1600	- 5.3	- 3.8	- 8.8	- 7.0
23	2100	0.5	800	- 3.9	- 3.0	-11.2	-10.6
24	2800	0.7	2400	- 8.1	- 6.2	- 5.6	- 4.2
25	3100	0.9	3000	-16.2	-12.0	- 8.8	- 7.8
26	3300	1.0	1300	-15.0	-12.1	-17.4	-15.1
27	3100	0.8	700	-15.8	-13.8	-14.6	-12.0
28	3000	0.7	2100	- 7.2	- 5.5	- 7.7	- 6.5
29	2700	0.7	2100	- 4.8	- 3.2	- 8.7	- 7.3
30	2600	0.6	1900	- 6.8	- 4.6	- 6.2	- 5.1
31	2700	0.6	1600	- 9.6	- 7.8	- 7.2	- 5.9
32	2800	0.8	1700	- 9.2	- 7.2	- 8.6	- 8.0
33	2700	0.7	1800	- 5.9	- 4.8	- 7.7	- 6.2
34	2600	0.6	1500	- 6.8	- 4.9	- 7.0	- 5.9
35	2800	0.7	1900	- 6.9	- 5.8	- 6.8	- 6.0
36	2900	0.8	2300	- 3.4	- 0.6	-13.8	-10.1
37	2800	0.8	2200	- 4.8	- 1.5	-15.6	-13.0
38	2900	0.7	1900	- 6.8	- 2.8	-14.0	-10.5
39	2800	0.8	1300	-10.0	- 8.5	- 9.0	- 7.3

As described in the foregoing, according to the present invention, 0.3 to 5.0 parts by weight of the above described particular additive is contained per 100 parts by weight of the above described main component having a particular composition, thereby to make it possible to provide a dielectric ceramic which can be sintered at a temperature of 1250° C and has sufficient dielectric properties.

Therefore, a base metal such as Ni can be used as a material constituting inner electrodes if the dielectric ceramic composition according to the present invention is used, thereby to make it possible to provide a low-cost multilayer capacitor.

Although the present invention has been described and illustrated in detail, it is clearly understood that the same is by way of illustration and example only and is not to be taken by way of limitation, the spirit and scope of the present invention being limited only by the terms of the appended claims.

CLAIMS:

1. A dielectric ceramic composition, which is characterized by containing 0.3 to 5.0 parts by weight of an additive composed of at least one of SiO_2 , Li_2O and B_2O_3 per 100 parts by weight of a main component expressed by a composition formula of $(1 - x - y - z - t) \text{BaTiO}_3 + x\text{CaZrO}_3 + y\text{MgO} + z\text{MnO} + t\text{Re}_2\text{O}_3$, where

$$x \leq 0.06$$

$$0.005 \leq y \leq 0.08$$

$$0.005 \leq z \leq 0.02$$

$$0.005 \leq t \leq 0.02$$

(In the composition formula, Re indicates at least one of Y, Gd, Dy, Ho, Er and Yb).

2. A dielectric ceramic composition according to claim 1, wherein

said x, y and z are in the respective ranges, that is, $0.01 \leq x \leq 0.04$, $0.02 \leq y \leq 0.08$ and $0.005 \leq z \leq 0.015$, and the content of said additive is 0.3 to 2.0 parts by weight.

3. A dielectric ceramic composition substantially as herein described.

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Patents Act 1977
Examiner's report to the Comptroller under
Section 17 (The Search Report)

Application number

9203362.0

Relevant Technical fields	Search Examiner
(i) UK CI (Edition K) C1J	MISS M M KELMAN
(ii) Int CI (Edition 5) C04B, H01G	
Databases (see over)	Date of Search
(i) UK Patent Office	10 APRIL 1992
(ii) ONLINE DATABASES: WPI	

Documents considered relevant following a search in respect of claims 1 TO 3

Category (see over)	Identity of document and relevant passages	Relevant to claim(s)
Y,P	EP 0431538 A2 (TAIYO YUDEN) 12 June 1991 see page 3, lines 48 to 50, and Examples	1 to 3
Y	EP 0385365 A2 (TAIYO YUDEN) see page 2, lines 50 to 52 and Examples	1 to 3
Y	EP 0385364 A2 (TAIYO YUDEN) see page 2, lines 50 to 52 and Examples	1 to 3
Y	EP 0187960 A2 (TAIYO YUDEN) see pages 2 and 3 and examples	1 to 3
Y	JP 62157603 A (KYOCERA)	1 to 3

Category	Identity of document and relevant passages	Relevant to claim(s)

Categories of documents

X: Document indicating lack of novelty or of inventive step.

Y: Document indicating lack of inventive step if combined with one or more other documents of the same category.

A: Document indicating technological background and/or state of the art.

P: Document published on or after the declared priority date but before the filing date of the present application.

E: Patent document published on or after, but with priority date earlier than, the filing date of the present application.

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Databases: The UK Patent Office database comprises classified collections of GB, EP, WO and US patent specifications as outlined periodically in the Official Journal (Patents). The on-line databases considered for search are also listed periodically in the Official Journal (Patents).